

PYROLYSIS AND HYDROPYROLYSIS OF COAL ASPHALTENES.

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Coal asphaltenes and their behaviour under typical coal liquefaction conditions have attracted considerable attention in recent years (1, and references therein), because of both their proposed role as intermediates in liquefaction processes and the potential problems presented by incomplete conversion of asphaltenes. The present work extends our previous studies on asphaltene fractions from coal extracts (1,2) to permit comparisons to be drawn between two asphaltenes, each derived from a hydrogenated-anthracene-oil extract of bituminous coal, but having significantly different carbon and oxygen contents.

Experimental.

The coal extract used was kindly supplied by the Coal Research Establishment, National Coal Board, Cheltenham, England. It was derived from Point of Ayr coal, extracted by a hydrogenated anthracene oil (Veba Oil).

Cylinder gases were obtained from the British Oxygen Company, and CoO-MoO₃ on AlO₃ from Strem Chemicals Inc. Details of the isolation of asphaltenes, by extraction into benzene followed by precipitation using n-pentane, are given elsewhere (1).

Pyrolysis and Hydropyrolysis Procedure.

Reactions were carried out in the stainless steel autoclave of 250 ml volume described previously (1), which was charged with asphaltene (1.5g) finely ground with catalyst (CoO-MoO₃ on AlO₃, 0.15g). After closure, the bomb was pressured to 87 bar (1300 p.s.i.) cold pressure with the appropriate gas (oxygen-free nitrogen for pyrolysis experiments, hydrogen for hydropyrolysis experiments). The temperature profiles of the reactions were complicated due to the considerable thermal mass of the bomb, and heat-up times varied between 40 mins. (to 200°C) and 60 mins. (to 425°C). Nominal reaction times are given as the number of minutes at the designated temperature, ignoring heat-up and cooling.

Fractionation of Products.

After cooling overnight, the bomb pressure was released by using a specially adapted two-stage needle-valve to leak the gases slowly into a train of three pre-weighed stainless-steel U-tubes loosely packed with dry molecular sieve (1/16in. pellets, type 3A), maintained at liquid nitrogen temperature. After reweighing, the traps were warmed to room temperature and the evaporating gases were transferred to an evacuated glass bulb fitted with a rubber septum to allow withdrawal of samples, using a gas-tight syringe, for injection onto a g.c. column. Following this out-gassing, the bomb was opened, benzene (20 ml) was added and the resulting slurry was coated onto cleaned glass beads (100-200 mesh, 100g) which were successively extracted, according to the method of Awadalla et al.(3), with n-pentane, benzene and pyridine. The bulked n-pentane solution was reduced in volume on a rotary evaporator to ca 20 mls weighed, then a 8µl

sample was withdrawn and injected onto the capillary g.c. column. The percentage of solvent (n-pentane and benzene) present was estimated from the g.c. trace and in this manner an approximate weight was arrived at for the n-pentane soluble product. The method was devised to minimise the under-estimation of light constituents such as methylated benzenes, which is inherent in any total drying of this fraction. The benzene and pyridine were removed from the asphaltene and preasphaltene solutions respectively, using a rotary evaporator and these products were dried in a vacuum oven (60°C , 3 hr) before weighing.

Analytical Procedures.

Elemental analyses were carried out by the University of Strathclyde Microanalytical Service. ^1H -n.m.r. spectra were recorded in deuterochloroform at 100 MHz on a Jeol MH100 spectrometer and (^1H) - ^{13}C -n.m.r. spectra in deuterochloroform at 50MHz using inverse-gated decoupling with a 10 sec. delay, and 100mg chromium acetylacetonate added to the sample.

Characterisation of gaseous products was carried out using a Hewlett-Packard model 5880A gas chromatograph fitted with a 2m, 3.2mm OD stainless-steel column packed with Porapak Q, and an oven temperature of 160°C . Nitrogen carrier gas and a flame ionisation detector were used, permitting identification of hydrocarbon gases only. No attempt was made to detect fixed gases. For the pentane-soluble products, a 50 m open tubular capillary column (fused silica with SE54 silicone gum as stationary phase) was used, with the oven temperature programmed from 50 – 265°C at $5^{\circ}\text{C min}^{-1}$ holding for 48 min. at 265°C . Further identification of the pentane-soluble material was carried out at the Institute of Offshore Engineering, Heriot-Watt University, using computerised g.c. - mass spectrometry with an INCOS data system. Samples were injected onto a 25m QV-101 fused silica column with the oven programmed from 50 – 260°C at $5^{\circ}\text{C min}^{-1}$, holding at 260°C for 48 min.

Pyrolysis Experiments.

Following our earlier work (1) on an asphaltene (A) with carbon content of over 91% and carbon aromaticity of 80%, we have carried out a series of experiments using a second asphaltene (B), with 87.1% carbon and 74% carbon aromaticity. Pyrolysis and hydropyrolysis reactions were carried out, to allow comparisons with the previous study on asphaltene A.

Pyrolysis at 425°C of asphaltene B in a mini-bomb reaction vessel (1) gave a product (see Table 2) consisting largely of asphaltene and pre-asphaltene (total 78%) with 9% n-pentane soluble material and 8% pyridine-insoluble material ("coke"). This compares with a rather higher coke content (23%) and a low percentage of n-pentane soluble material (3–4%) in the product from asphaltene A, confirming the expectation that the asphaltene of lower carbon content and aromaticity would give rise to more tractable products. However, the results of this kind of pyrolysis experiment are extremely sensitive to changes in the conditions of the reaction. Thus, when asphaltene B was pyrolysed at 425°C in the Parr bomb under nitrogen pressure, in conditions of geometry and pressure

mimicking those used in the hydrogenation studies, a quite different product was obtained, consisting largely of gases (defined as C_1-C_4 hydrocarbons plus H_2S and other minor constituents) and coke. Only 6% was recovered as asphaltene or preasphaltene. Clearly, the changes in geometry, pressure and true reaction time combined to produce a result quite different from that obtained in the mini-bomb. Bearing this in mind, the data from the Parr bomb pyrolyses are used below as the basis for comparisons with hydropyrolysis experiments.

Hydropyrolysis Experiments.

Pyrolysis at $425^\circ C$ of asphaltene B under hydrogen pressure in the presence of a hydrogenation catalyst gave product distributions shown in Fig. 1. Even at the shortest reaction time (10 min) conversion to over 40% pentane-soluble material was achieved, with less than 20% recovery of asphaltene. After 1 hour at $425^\circ C$, only 12% asphaltene was recovered while the pentane-soluble yield was maintained at $> 40\%$. However, the conversion to gas in the latter case was higher than at the shorter reaction time, the level of preasphaltenes and heavier products remaining low. This compares with much lower conversion of asphaltene A under identical conditions (see Fig. 2), accompanied by larger amounts of preasphaltene and coke. In general, for both asphaltenes, pyrolysis under nitrogen led to gas and heavy preasphaltenes and cokes as the major products - a result that can be regarded as a disproportionation of the starting asphaltene. Similar reactions under hydrogen pressure led to increased recovery of liquids and asphaltene, suggesting stabilisation of reactive fragments by hydrogen, but significant amounts of gas were still generated, particularly from asphaltene A, at longer reaction times.

Product Analysis.

Elemental analysis and ^{13}C -n.m.r. spectroscopy (see Table 1) revealed no significant differences in carbon content or carbon aromaticity between starting asphaltene and recovered asphaltene in any of the reactions using asphaltene A. There was, however, an increase in aromaticity, as measured from 1H n.m.r. spectra, of 5% in hydropyrolysis and 9% in pyrolysis. A smaller increase (2% and 4% respectively) in hydrogen aromaticity was observed in the product asphaltene from the more reactive asphaltene B. This presumably reflects the pyrolytic loss, under all the conditions studied, of aliphatic structures present in the parent asphaltene and is reflected in the aliphatic content of the n-pentane soluble liquid products. The overall hydrogen/carbon ratio is also reduced in both asphaltenes recovered from pyrolysis, confirming the pyrolytic loss of hydrogen-rich material.

Differential Pulse Voltammetry [D.P.V.] (4) and Size Exclusion Chromatography [S.E.C.] on asphaltene B and its hydropyrolysis products indicate a slight shift to lower values for the molecular-weight distribution of the asphaltene recovered after reaction compared with asphaltene B itself. This is accompanied by a marked decrease in the D.P.V. peaks assigned to pyrene, anthracene and other polyaromatic structures, which can be characterised by D.P.V. even when substituted and linked together in larger molecules. Diaromatics such as naphthalene remain very much in evidence, however (5). Taken together with the n.m.r. spectroscopic evidence, this suggests that hydrogenation leads to a loss of purely aliphatic side-chains and partial hydrogenation of large polyaromatic structures to leave an asphaltene consisting largely

of diaromatic and monoaromatic centres (the latter not observable by D.P.V.) linked by methylenic bridges that constitute most of the remaining aliphatic character.

A detailed analysis of the composition of the n-pentane soluble products was carried out using gas chromatography-mass spectrometry. We have discussed previously (1,2) the identification in the asphaltene A products of a series of n-alkanes ranging up to C_{29} in the pyrolysis case, and to C_{14} in the hydropyrolysis case. A similar series of n-alkanes was found in the asphaltene B liquid products, together with a range of branched alkanes including traces of isoprenoids such as pristane (C_{17}) and phytane (C_{18}). Altogether the aliphatics (separated by column chromatography, see ref. 6) made up approximately 10% by weight of the B hydrophrolystate. A similar spectrum of aliphatic material was identified in the pyrolysate produced under nitrogen, supporting the suggestion that the majority of the alkanes originate as primary pyrolysis products. The remaining 90% of the liquid product is made up of aromatic hydrocarbons together with a trace (>2%) of polar materials, predominantly alkyl phenols and indoles. No sulphur-containing species has been identified in the liquid product, and most of the sulphur appears to be converted to H_2S .

The composition of the aromatic hydrocarbons that form the bulk of the liquid product - and hence some 40% of the total products - is of interest and has been analysed in some detail. Phenanthrene, pyrene and anthracene peaks are prominent in the D.P.V. trace of the pentane-soluble hydropyrolysate (5) and gas chromatography confirms that the single largest component in the mixture is phenanthrene which, together with other polyaromatics such as pyrene and fluoranthene, dominates the liquid product. This is qualitatively in accord with thermodynamic predictions (7). Both the pyrolysate and hydropyrolysate also contain a wide range of alkyl-benzenes, which may therefore be primary pyrolysis products, and a significant amount of dibenzofuran, possibly formed by condensation of neighbouring phenolic functions. The low level of phenolic material in the pentane-soluble fraction even of the pyrolysate was surprising in the light of earlier results (1) and the fate of the oxygen, phenolic and non-phenolic, requires further study. The hydropyrolysate also contains a range of partially hydrogenated polyaromatics arising from the fully condensed forms produced by pyrolysis. Phenanthrene and pyrene, in particular, are present in association with several hydrogenated forms in sufficient amounts to allow quantitation from capillary g.c. traces (see Figs. 3,4). Comparison of these results with "model-compound" studies of phenanthrene and pyrene hydrogenation (5,6) shows that, in the complex matrix present during asphaltene hydrogenation, the formation of perhydro-species is completely suppressed. Indeed, dihydrophenanthrene and dihydropyrene are the dominant hydrogenated species even at long reaction times. It is hard to envisage complete hydrogenation of these polyaromatic species under any realistic time-temperature-pressure regime. This is partly attributable to the tendency of some of the hydrogenated species to act as hydrogen donors, so that the asphaltene matrix becomes, as it were, a "hydrogen sink", inhibiting stepwise progress along a hydrogenation pathway. We have also found, and confirmed in separate pyrene studies (10) under similar conditions, that at the temperatures we have used a significant amount of pyrene breaks down, presumably via the 1,2-dihydro-form, to 4,5-dimethylphenanthrene which resists further hydrogenation. The character of the pentane-soluble pyrolysate and hydropyrolysate derived from asphaltene A does not differ greatly from that discussed here.

Further hydrogenation studies currently in progress will allow us to build up a more complete picture of the factors at work in asphaltene hydrogenation. However, we can summarise our conclusions to date as follows:

1. The general pattern of asphaltene conversion, viz., to gas and heavy, intractable materials on pyrolysis and to gas and liquids under hydropyrolysis conditions, remains the same for both average and high-carbon asphaltenes, but the extent of conversion to liquids upon hydropyrolysis is limited when the carbon content is high.
2. The aliphatic content of the liquids formed is low, not exceeding 10%, and arises from aliphatic groups present in the reactant asphaltene. The aliphatic content in the asphaltenes recovered after reaction is probably largely in the form of bridging methylenic functions.
3. The distribution of hydrogenated species in the highly aromatic liquid products indicates that complete hydrogenation of the polyaromatics produced in pyrolysis is difficult in the presence of a complex, hydrogen-hungry matrix. Conclusions drawn from model compound studies, while useful, must be used with caution in interpreting or predicting the behaviour of coal-derived materials.

References.

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Table 1 : Analytical and Spectroscopic Data for
Various Coal-Derived Asphaltenes.

	Starting Material		Recovered from Pyrolysis		Recovered from Hydropyrolysis	
	A	B	A	B	A	B
% C	91.9	87.1	92.1	88.2	92.7	88.2
% H	5.8	6.1	5.3	5.9	5.4	6.1
% N	1.0	1.4	trace	1.5	trace	1.5
(direct) % O	0.8	4.1	-	-	-	-
% S	not detected	0.6	-	-	-	-
% Carom	80	74	-	74	79	75
% Harom	44	42	53	46	49	45
H/C	.75	.81	.70	0.80	.70	.83

Table 2 : Yield Structure for Asphaltene Pyrolysis.

	Asphaltene A		Asphaltene B	
	mini-bomb	Parr bomb	mini-bomb	Parr bomb
% gas)	28	< 5	35
% pentane sol.) 5 total	15	9	17
% asphaltene	53	3	44	4
% preasphaltene	19	3	34	2
% coke	23	47	8	36

Figure 1

425°C Hydrogenation of Asphaltene B:

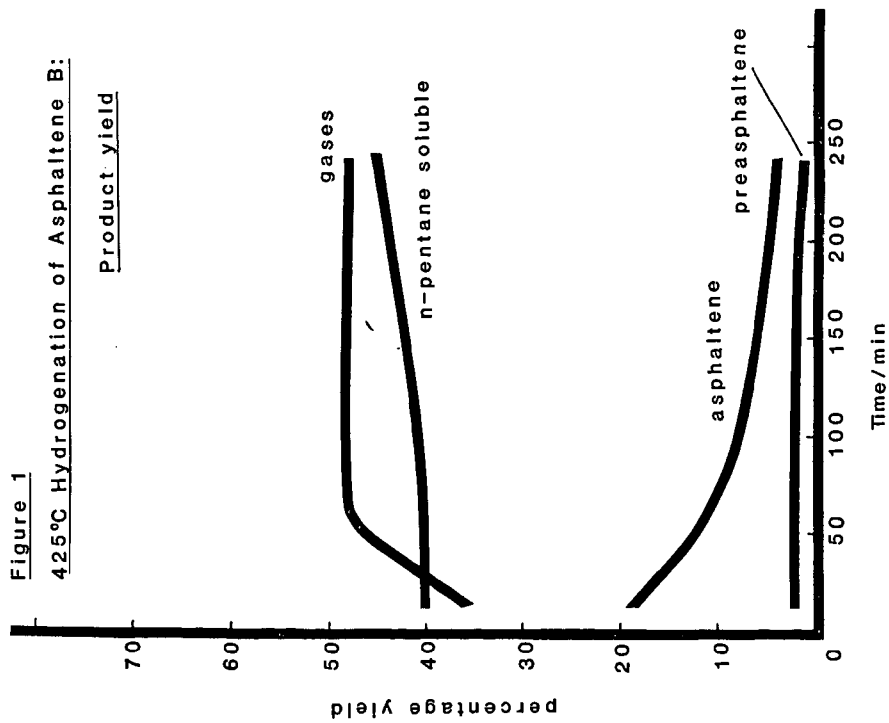


Figure 2

425°C Hydrogenation of Asphaltene A:

